The Role of "Frequency Factors" in Determining the Difference Between Low- and High-voltage Mass Spectra

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Some advantages in determining the low-voltage mass spectra (usually using 10—16 ev electrons) of organic compounds have recently been emphasised.[1–3] While the importance of energetics in determining the difference between spectra of complex molecules at 70 ev and at low beam energies has been considered,[2] the role of frequency factors in this context has not been discussed.

In its simplest form, the quasi-equilibrium theory of mass spectra relates the rate constant k for the decomposition of an ion with its internal energy E as indicated in the equation:

$$k = \nu \left(\frac{E - E^0}{E}\right)^{N-1}$$

where E^0 is the activation energy for decomposition, N is the number of effective harmonic oscillators, and ν may be regarded as a frequency factor.[4] The number of effective harmonic oscillators is considerably less than the total number of internal degrees of freedom in the ion,[5] but the important point is that for the organic molecules which we discuss, the power to which $(E - E^0)/E$ is raised is large. Consider two competing unimolecular reactions occurring from a single molecular ion and associate with these reactions parameters k_1, ν_1, E^0_1 and k_2, ν_2, E^0_2. For a hypothetical case in which E corresponds to 10 quanta, E^0_1 and E^0_2 to 9 and 7 quanta, the term $(E - E^0_2/E)^{N-1}$ will be much larger than $(E - E^0_1/E)^{N-1}$ and, given ν_1 and ν_2 of similar magnitude, $k_2 \gg k_1$. However, if $\nu_2 \ll \nu_1$, the situation $k_2 \simeq k_1$ may arise. Since the value of E relative to E^0_1 and E^0_2 was chosen to simulate an extreme of low-voltage behaviour, we see here a case where similar ion abundances will result from the competing reactions at low voltage because the process of lower activation energy has a lower frequency factor. However, in a 70 ev spectrum, values of E much greater than E^0_1 or E^0_2 will be heavily weighted, and therefore the ratio of the terms $(E - E^0_2/E)^{N-1}$ and $(E - E^0_1/E)^{N-1}$ will be much less, and if $\nu_2 \ll \nu_1$, then at 70 ev we have $k_1 > k_2$. It will frequently be the case that rearrangement reactions will have lower frequency factors than simple bond cleavages. When such rearrangement reactions have relatively low activation energies, they will compete most successfully with simple bond cleavages in low-voltage spectra. In general terms, the rise of k with E will be smaller for rearrangement reactions with low frequency factors, given an activation energy which is similar to that for a competing simple bond dissociation.

A perusal of spectra determined in our laboratory, and of literature data, confirms the increasing importance of hydrogen rearrangement reactions in many low-voltage spectra; relevant data are summarised in the Table.

The method of quoting relative abundances to give a crude measure of relative reaction rates suffers from the disadvantage that further rates of decomposition of the two fragment ions are probably different. Nevertheless, the overall trend is clear; namely, that in the cases studied, daughter ions of moderate abundance produced by rearrangement reactions at 70 ev, become much more abundant in low-voltage spectra (relative to ions produced by simple dissociation). The data for the ketones (1)—(4) and the ester (8) exemplify the increasing importance of McLafferty rearrangement relative to simple bond cleavages at low ev. In the ketones (5) and (6), benzylic cleavage gives rise to the base peak ($C_7H_7^+$) at 70 ev, but at low ev rearrangement reactions (especially loss of water from M^+) are dominant.[6] The esters (9) and (11) give peaks of similar abundance due to loss of an alkanol molecule or of an alkoxy-radical at 70 ev, but the loss of the alkanol is dominant at low voltage. It is apparent that for a rearrangement reaction with a low frequency factor to compete successfully at 70 ev with a simple dissociation of high frequency factor, the rearrangement process must have a lower energy of activation.† In these cases it will obviously be possible to remove the simple bond cleavage completely at even lower voltages than those referred to in the Table.

The data for (13)—(15) refer to double hydrogen rearrangements, where the effect of frequency factors might well be even larger. This is true for the ketones (13) and (14), in which the "McLafferty-plus-one rearrangement"[7] ($M^+ - C_nH_{2n-1}$) becomes

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† Positive evidence for a low frequency factor for a rearrangement process is available from the presence of an intense "metastable peak" for the process (W. Chupka, *J. Chem. Phys.*, 1959, **30**, 191). For example, for the ester (9), there is no "metastable peak" for loss of a methoxy-radical, but an abundant "metastable" peak for the loss of methanol.

Relative abundances of ions produced by simple dissociation and rearrangement reactions at low voltage (10—16 ev) *and at* 70 ev

Compound	Processes	Abundance ratio[a] Low ev	Abundance ratio[a] 70 ev	m^*[b]
(1) Pr^{n}COMe	$M^+ - C_2H_4 : M^+ - \mathrm{Me}$	2·5 : 1·0	1·0 : 1·1	*
(2) Pr^{n}COPh	$M^+ - C_2H_4 : \mathrm{PhCO}^+$	1·0 : 1·6	1·0 : 17	*
(3) Bu^{n}COPh	$M^+ - C_3H_6 : \mathrm{PhCO}^+$	10 : 1·0	1·0 : 2·0	*
(4) Bu^{i}COPh	$M^+ - C_3H_6 : \mathrm{PhCO}^+$	1·4 : 1·0	1·0 : 5·0	*
(5) $\mathrm{MeCO[CH_2]_4Ph}$[6]	$M^+ - H_2O : C_7H_7^+$	2·0 : 1·0	1·0 : 13	*
(6) $\mathrm{MeCO[CH_2]_5Ph}$[6]	$M^+ - H_2O : C_7H_7^+$	4·0 : 1·0	1·0 : 3·3	*
(7) Bu^{n}Ph	$M^+ - C_3H_6 : M^+ - C_3H_7$	13 : 1·0	1·0 : 2·0	*
(8) Pr^n$\mathrm{CO_2Me}$	$M^+ - C_2H_4 : M^+ - \mathrm{OMe}$	4·0 : 1·0	1·3 : 1·0	*
(9) $\mathrm{Ph[CH_2]_3CO_2Me}$	$M^+ - \mathrm{MeOH} : M^+ - \mathrm{OMe}$	14 : 1·0	1·0 : 1·0	*
(10) $\mathrm{Cl[CH_2]_3CO_2Me}$	$M^+ - \mathrm{HCl} : M^+ - \mathrm{Cl}$	1·0 : 1·0	1·0 : 10	
(11) $\mathrm{MeCOCH_2CO_2Et}$	$M^+ - \mathrm{EtOH} : M^+ - \mathrm{OEt}$	22 : 1·0	1·0 : 2·0	
(12) $\mathrm{PhSO_2Cl}$	$M^+ - SO_2 : M^+ - \mathrm{Cl}$	12 : 1·0	1·0 : 6·2	
(13) $\mathrm{EtCO[CH_2]_4Me}$[7]	$M^+ - C_4H_7 : M^+ - C_4H_8$	1·0 : 3·5	<1·0 : 8·0	
(14) $\mathrm{MeCO[CH_2]_5Me}$[7]	$M^+ - C_5H_9 : M^+ - C_5H_{10}$	1·0 : 1·05	~1·0 : 7·0	
(15) $\mathrm{EtO[CH_2]_5Me}$[8]	$\mathrm{Et\overset{+}{O}H_2} : C_6H_{13}^+$	7·5 : 1·0	2·7 : 1·0	

[a] In the quoted abundance ratios, the value for the less abundant ion is arbitrarily taken as 1·0 units.

[b] An asterisk indicates an appropriate "metastable peak" to establish the occurrence of the rearrangement process in one step.

more abundant relative to the normal McLafferty rearrangement ($M^+ - C_nH_{2n}$) at low voltage.[7] In the spectrum of ethyl n-hexyl ether (15), the peak due to protonated ethanol (formed by a double hydrogen rearrangement) rises rapidly in intensity relative to simple cleavage products.[8] In perfect accord with our postulate, is the observation[9] that the double hydrogen rearrangement reaction which affords protonated propionic acid (*m/e* 75) from butyl propionate gives rise to the base peak at 12 ev, although *m/e* 75 is only 25% of the base peak *m/e* 57, EtCO$^+$) at 70 ev. It is of considerable interest that these double hydrogen rearrangement reactions have such low activation energies.

An important application of the approach may be found in uncovering rearrangement processes associated with *apparent* single bond cleavages. For example, methyl cinnamate affords $M^+ - \mathrm{H}$ and $M^+ - \mathrm{OMe}$ ions in the abundance ratio 1·0 : 5·5 at 70 ev.‡ If it were assumed that these reactions had very similar frequency factors, then one would have to conclude that the activation energy for loss of methoxyl was smaller. However, the relative abundances change drastically at low ev (*e.g.* 2·0 : 1·0 at a nominal 11 ev) and the appearance potential for loss of a hydrogen radical is in fact lower. Therefore, the loss of a hydrogen radical has a lower frequency factor,§ which suggests that its elimination may be associated with a rearrangement process. Indeed, a previous deuterium labelling study indicated that the loss of a hydrogen radical was associated with cyclisation of the ester carbonyl on to the aromatic ring.[10]

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‡ There is no evidence for further decomposition of the $M - \mathrm{H}$ ion, but the $M - \mathrm{OMe}$ ion does undergo further loss of CO at 70 ev.

§ An alternative explanation, invoking the presence of isolated electronic states, is possible, but seems less probable.

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[9] Ref. **3**, p. 184.

[10] J. Ronayne, D. H. Williams, and J. H. Bowie, *J. Amer. Chem. Soc.*, 1966, **88**, 4980.